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Variation of Line Width with Rotational State and Temperature in the Microwave Spectrum of OCS*

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The earlier measurements on the self-broadening of OCS rotational transitions by Johnson and Slager have been extended. Measurements have been made at constant pressure on seven rotational transitions in the ground vibrational state from $J=3\rightarrow 4$ to $J=15\rightarrow 16$ and at dry ice and room temperatures. The data have been interpreted by a simple theory which assumes a constant contribution to line width from dipole-dipole interactions and an additional J-dependent contribution from rotational resonance interactions. Empirically determined temperature dependence is introduced for each contribution. This interpretation, when fit to the observed line widths, $\Delta\nu$ results in the expression

$$\Delta\nu=\frac{1815}{T}+0.00321T^{\frac{1}{2}}(J+1)^2e^{-hBJ(J+1)/kT}\ \text{Mc/sec}$$

at 1-mm Hg pressure. The collision diameters for OCS are found to be approximately linear functions of the rotational state and independent of temperature.

INTRODUCTION

WHILE the general aspects are understood of the process by which microwave spectral lines are broadened by molecular collisions, there does not exist complete understanding of the details of these mechanisms. Theoretical explanations have been particularly hampered by a lack of sufficient experimental information on collision broadening. The data reported herein represent an attempt to provide further experimental information on the broadening process.

Collision broadening of microwave spectral lines was first reported in detail by Bleaney and Penrose[1] who measured the self-broadening of ammonia as a function of transition. Their results were later verified by Potter, Bushkovitch, and Rouse.[2] Theoretical explanations of the results of Bleaney and Penrose were immediately attempted by Margenau[3] and by Anderson.[4]

While considerable information was subsequently published on collision broadening by foreign gases, the next self-broadening data reported were on oxygen. Anderson, Smith, and Gordy,[5] Gokhale and Standberg,[6] and Artman and Gordon[7] gave experimental evidence for the variation of line width with rotational transition in oxygen. At about the same time Leslie,[8] Margenau,[9] and Mizushima[10] published new theories to explain collision broadening. The most recent experimental data on the effect of rotational transitions upon self-broadening were reported by Johnson and Slager,[11] and Feeny, Lackner, Moser, and Smith[12] who studied this behavior in the OCS molecule.

Observation of the variation of line width with temperature has been limited, however experimental data has been given by Howard and Smith for ammonia,[13] Beringer and Castle for oxygen,[14] Johnson and Slager,[11] and Feeny *et al.*[12] for OCS, and Hill and Gordy for oxygen.[15]

Experimental observations of collision self-broadening should take into account the following factors: (1) the molecule being observed should be simple, preferably diatomic or at least linear; (2) rotational transitions of the electric dipole type should be observed; (3) measurements should be made over a wide range of transitions; (4) temperature dependence of line width should be determined for a constant number of molecules and also for constant pressure. The chief experimental difficulty in line-width measurements is the third point. Observation of a large number of transitions usually requires measurements over a wide band of wavelengths extending into the millimeter wavelength region. Ammonia and oxygen, however, are exceptions to this because of the peculiar origin of their microwave spectra. The ammonia spectrum is of the inversion type, while the oxygen spectrum arises from spin-spin interactions of the unneutralized electrons in this paramagnetic molecule. As a result the microwave spectrum of ammonia contains many

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[1] B. Bleaney and R. P. Penrose, Proc. Phys. Soc. (London) **B59**, 418 (1947).

[2] Potter, Bushkovitch, and Rouse, Phys. Rev. **83**, 987 (1951).

[3] H. Margenau, Phys. Rev. **76**, 121 (1949).

[4] P. W. Anderson, Phys. Rev. **76**, 647 (1949); **80**, 511 (1950).

[5] Anderson, Smith, and Gordy, Phys. Rev. **82**, 264 (1951); **87**, 561 (1952).

[6] B. V. Gokhale and M. W. P. Strandberg, Phys. Rev. **84**, 844 (1951).

[7] J. O. Artman and J. P. Gordon, Phys. Rev. **87**, 227 (1952).

[8] D. C. M. Leslie, Phil. Mag. **42**, 37 (1951).

[9] H. Margenau, Phys. Rev. **82**, 156 (1951).

[10] M. Mizushima, Phys. Rev. **74**, 705 (1948); **83**, 94 (1951); **84**, 362 (1951).

[11] C. M. Johnson and D. M. Slager, Phys. Rev. **87**, 677 (1952).

[12] Feeny, Lackner, Moser, and Smith, J. Chem. Phys. **22**, 79 (1954).

[13] R. R. Howard and W. V. Smith, Phys. Rev. **77**, 840 (1950).

[14] R. Beringer and J. G. Castle, Phys. Rev. **81**, 82 (1951).

[15] R. M. Hill and W. Gordy, Phys. Rev. **93**, 1019 (1954).

transitions over a relatively short wavelength region from 1.3 to 1.8 cm while the oxygen spectrum is confined primarily to the region from 4.5 to 5.6 mm. With these two molecules it is then possible to measure line widths for a number of transitions in a narrow wavelength region, thus considerably reducing the experimental difficulties. For this reason the first measurements of line width as a function of transition were performed on ammonia and oxygen.

Despite the desirable experimental features of measurements on ammonia and oxygen, it is difficult to arrive at a simple theoretical explanation of the observed results because of the unusual origin of these spectra. For this reason it is desirable to make measurements on molecules of simple structure whose absorptions arise from simple rotational transitions. Data from such measurements should prove of value in theoretical explanation of broadening effects. Accordingly, the sulfur carbonyl molecule was chosen for this investigation. Earlier measurements on this molecule[11,12] indicated the dependence of line width on rotational transition and temperature. The development of experimental techniques for the generation of wavelengths down to one millimeter[16,17] has made possible the extension of line-width measurements to higher rotational transitions.

APPARATUS AND PROCEDURE

The difficulties of measuring the half-intensity half-widths of spectral lines, according to the definition of the line width, are alleviated by making accurate measurements of the inflection points of the intensity curve and relating these points to the line width. Location of inflection points may be determined by observing the derivative of the intensity curve with respect to frequency. If one assumes small absorption by the molecule, it is easily demonstrated that the frequency separation of the inflection points $2\delta\nu$ is related to the line width $\Delta\nu$ defined as the half-width at half-intensity by $\Delta\nu=\sqrt{3}\delta\nu$. In the following section, however, it will be shown that this result is not accurate for the case where the molecule absorbs an appreciable amount of the incident energy. It will accordingly, be modified to correct for this effect.

The technique of the measurement of line widths by the derivative method has been widely used.[5,11,12,18] For weak transitions the derivative shape is usually recorded, however, it is more convenient to use cathode-ray oscilloscope presentation for direct measurement.

A block diagram of the apparatus is given in Fig. 1. The microwave equipment consists of a K-band klystron which supplies energy to a crystal multiplier,[17] here used to generate energy as high as the eighth harmonic of the klystron output. By means of appropriate transition sections this energy, at wavelengths down to 1.54 mm, is applied to a wave guide absorption cell. The transmitted energy is detected by a special silicon detector.[17] In the present work three different absorption cells were employed. Two were K-band cells of lengths 100 cm and 10 cm, and one was a G-band cell of length 17 cm. The shorter K-band cell was so constructed that it could be completely immersed in a dry ice-acetone bath, so that all absorbing molecules would be at a temperature of 195°K.

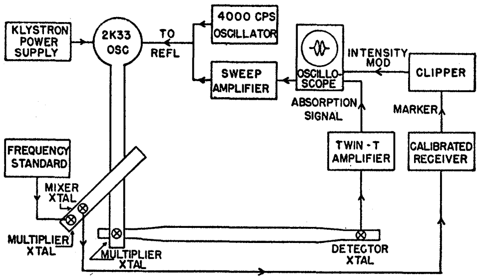

FIG. 1. Block diagram of the apparatus.

The first derivative of the line shape is obtained by superimposing a small (~0.1v) sinusoidal voltage on the sawtooth modulation applied to the klystron reflector. This frequency modulated klystron output results in an absorption signal incident on the detector crystal which is proportional to the slope of the line intensity curve at the unmodulated frequency of the klystron. The smaller the frequency modulation, the more closely the regulating signal will represent the first derivative of the line shape.

Earlier techniques used 100 kc/sec sinusoidal reflector modulation.[11,18] The signal emergent from the crystal detector, containing a 100 kc/sec component, was amplified in a communication receiver and then detected. The signal which resulted was proportional to the absolute value of the first derivative of the intensity. This technique was initially employed for the present measurements, but was soon abandoned for several reasons. First, for the very weak, high-transition lines, this method was found extremely insensitive. Second, the line width was found to vary with frequency modulation amplitude. Third, the line width varied with the sweep rate of the sawtooth modulation. In an effort to eliminate these deficiencies, particularly the loss of sensitivity, modifications were made to this early technique. First, a frequency modulation of 4 kc/sec was used. Second, the amplified crystal output was not detected. The result was a significant increase in sensitivity, so much so as to exceed the signal strength of the line seen by conventional video search techniques.[19] The crystal detector signal, containing a 4 kc/sec component was

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[16] W. C. King and W. Gordy, Phys. Rev. **90**, 319 (1953).

[17] W. C. King and W. Gordy, Phys. Rev. **93**, 407 (1954).

[18] R. R. Howard and W. V. Smith, Phys. Rev. **79**, 128 (1950).

[19] This modulation method is not recommended as a search technique, since the adjustment of modulation voltage amplitude and of amplifier frequency is critical and can only be made on a line already known to exist. The method is similar to that described by W. Gordy and M. Kessler, Phys. Rev. **72**, 644 (1947).

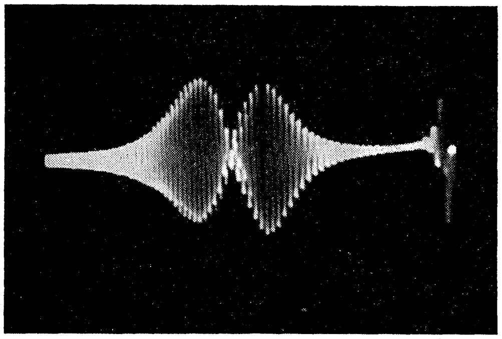

FIG. 2. Photograph of the cathode-ray oscilloscope presentation of the $J=7\rightarrow 8$ transition occurring at 97 301.32 Mc/sec, the fourth harmonic of the klystron frequency.

amplified in an M.I.T. Radiation Laboratory type TAA-16B twin-T amplifier tuned for 4 kc/sec. The undetected output of this amplifier was fed directly to the vertical deflection plates of a cathode-ray oscilloscope. The resultant pattern is seen in Fig. 2. The oscillating portion occurs at a 4 kc/sec rate and the envelope of this oscillation is the first derivative of the line shape. Feeny *et al.*,[12] investigating the effect of modulation frequency on observed line width, have shown that the use of frequencies higher than 10 kc/sec produces a systematic increase in line width with frequency increase. Their data indicate that the use of 4 kc/sec modulation frequency results in a good approximation to the true measured line width, $\delta\nu$, as the modulation frequency approaches zero. Thus it is unnecessary to extrapolate line width measurements to zero modulation frequency as they do.

While the low-frequency modulation technique greatly improved sensitivity and eliminated the effect of sweep rate on line width, the effect of frequency modulation amplitude on line width still remained. Accordingly measurements were made on the effect of modulation amplitude on line width. The results are shown in Fig. 3. The parabolic shape of the curve indicates that measurements on line width made using modulation amplitudes below 0.1v rms will evidence an inherent systematic broadening error of less than 1 percent of the true line width. Consequently all measurements were made using the minimum possible modulating voltage and in no case did this exceed 0.1v rms.

The measurement of the frequency separation of the inflection points was achieved through the use of a movable marker superimposed as an intensity modulation of the cathode-ray trace of the derivative of the absorption line. This marker was derived from the beat note produced between a frequency standard output and the sawtooth frequency-swept klystron. This beat note, of about 25 Mc/sec, was amplified in a communication receiver. The receiver output, which was used to blank the oscilloscope trace, was applied to the oscilloscope through a clipping circuit which made possible width control of the blanked-out portion of the trace. This marker may be seen in Fig. 2. The position of the marker could be changed by tuning the receiver. In making the width measurement, the marker position was measured as a function of receiver dial reading as the marker was placed on top of each of the maxima of the derivative curve. The receiver dial was then calibrated by observing the location of calibration points separated by 1 Mc/sec. Interpolation was used between calibration points.

The procedure used in making a measurement was as follows: (1) By observation of the line, the amplitude of the modulating voltage was set to the smallest possible value less than 0.1v rms. It was carefully determined that this represented the minimum line width. (2) Measurement of pressure ($\sim 10^{-1}$ mm) was made with a McLeod gauge and this used to calibrate a vacuum thermocouple gauge. (3) Ten to twenty width measurements were made. (4) The receiver was calibrated. (5) Remeasurement was made of the pressure. (6) Absorption cell temperature was observed. (7) Dry ice was placed around the absorption cell and the first six steps were repeated.

RESULTS

As mentioned in the preceding section it is necessary to correct the observed line widths, $\delta\nu$, for the effects of large absorption by the molecules.[20] At the higher frequencies and with long absorption cells energy absorption by the molecules becomes very large, approaching total absorption of the incident energy at the line center. Because of this fact the shape of the absorption line becomes distorted from the usual Lorentz shape. The wings of the line absorb relatively more energy and the line becomes broadened and flattened near its center. The method of correcting for this effect is given in the Appendix.

The results of the measurements are given in Table I. The line widths are expressed in terms of the width the line would have if the pressure were 1 mm Hg. This form of expression is based upon the assumption that the line width is directly proportional to pressure. This is an established experimental fact for this range of pressures.[5,12,18] Reduction of data to this expression is necessary because of the fact that most of the measurements were made at different times, with different pressures, and with different absorption cells. The data are shown graphically in Fig. 4.

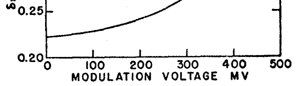

FIG. 3. Observed line width as a function of modulation amplitude.

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[20] The author is indebted to Dr. W. V. Smith for pointing out the need for this correction.

TABLE I. Transition frequencies, line widths, and collision diameters for the OCS molecule. Frequencies are those of King and Gordy (see reference 17). Figures in the Cell column designate wave-guide size (*K*- or *G*-band) and length of absorption cell in cm. Measurements designated *K*-214 are those of Johnson and Slager (see reference 11), and *F*, those of Feeny, *et al.* (see reference 12). Line-width corrections are calculated from Eq. (10). Corrected line widths, divided by pressure, express results uniformly at 1-mm Hg pressure. Line width values in parentheses are mean values for that temperature. Collision diameters are calculated from mean line-width. (Note: Incomplete immersion of the *G*-17 cell in dry ice caused slight narrowing of lines. Collision diameters at 195°K are based only on *K*-10 data.)

J transition	Frequency Mc/sec	Cell	Temperature °K	Pressure (10^{-2} mm Hg)	Observed line width $\sqrt{3}\delta\nu$ kc/sec	Line width correction kc/sec	Corrected line width (constant pressure)		Collision diameter *b*(A)
							(Mc/sec)	per mm	
1→2	24 325.92	*K*-214	300	10.0	610	—	6.0	(6.2)	9.2
		F	300				6.4		
		F	195				9.6		10.2
3→4	48 651.62	*K*-214	300	13.0	935	21	7.0	(7.0)	9.8
		K-100	307	7.89	565	6	7.1		
5→6	72 976.80	*K*-214	300	10.0	823	52	7.7	(7.8)	10.3
		K-100	304	10.2	839	26	8.0		
7→8	97 301.32	*K*-214	300	11.0	1083	117	8.8	(9.5)	11.4
		K-100	303	6.48	537	37	7.7		
		G-17	295	3.64	424	4	11.5		
		K-10	303	6.15	610	4	9.9		
		G-17	195	3.67	409	14	10.8		11.2
		K-10	195	5.57	644	12	11.3		
9→10	121 624.64	*K*-100	301	6.48	689	73	9.5	(10.5)	11.9
		G-17	295	3.69	433	8	11.5		
		K-10	303	6.12	655	7	10.6		
		G-17	195	3.72	445	26	11.3		11.9
		K-10	195	5.57	737	22	12.8		
11→12	145 946.80	*K*-100	302	6.47	805	120	10.6	(12.4)	13.0
		G-17	295	3.70	488	13	12.8		
		K-10	306	5.66	797	10	13.9		
		G-17	195	3.62	527	41	13.4		12.7
		K-10	195	5.41	823	35	14.6		
13→14	170 267.45	*K*-100	303	3.49	584	97	13.9	(14.5)	14.0
		G-17	295	3.91	591	20	14.6		
		K-10	306	5.50	840	15	15.0		
		G-17	195	3.82	620	63	14.6		12.5
		K-10	195	5.51	830	52	14.1		
15→16	194 586.35	*G*-17	295	3.06	551	23	17.3	(17.3)	15.3
		K-10	306	6.10	1078	23	17.3		
		G-17	195	3.06	585	68	16.9		13.9
		K-10	195	6.19	1140	78	17.4		

As correction for line broadening resulting from molecular collisions with the walls of the absorption cell, the formula of Danos and Geschwind[21] was considered. When these corrections were applied to the data it appeared that, for the smaller *G*-band wave guide, the corrections were excessive and resulted in discrepancies between data obtained on the same transitions but in different absorption cells. Since, without considering wall collisions, the measurements in the two different size wave guides agreed fairly well, these corrections were not applied.

Since the mechanism of line broadening is a collision process, it is informative to determine collision diameters according to the kinetic theory. This has been done by using the expression[18]

$$\Delta\nu=\tfrac{1}{2}\sqrt{2}n\bar{v}b^2,$$

where n is the number of molecules per cm^3, $\bar{v}$ is the mean relative velocity of the molecules, and b is the collision diameter of the molecule (which may here be considered as the molecular diameter[22]). The mean relative velocity of the molecules, $\bar{v}$, is given by[23]

$$\bar{v}=2(2R_MT/\pi M)^{\frac{1}{2}},$$

where $R_M=8.31\times10^7$ erg/°C-mole, T is the absolute temperature, and M is the molecular weight of OCS.

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[21] M. Danos and S. Geschwind, Phys. Rev. **91**, 1159 (1953).

[22] E. H. Kennard, *Kinetic Theory of Gases* (McGraw-Hill Book Company, Inc., New York, 1937), p. 103.

[23] See reference 22, pp. 45 and 112.

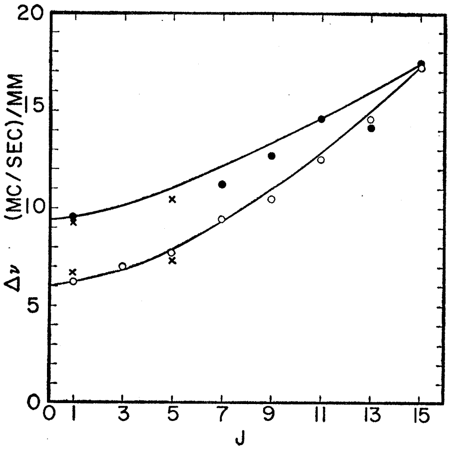

FIG. 4. Line width as a function of transition and temperature. Solid points represent experimental observations at dry ice temperature (195°K). Circles are data at room temperature (300°K). The curves are plotted from Eq. (5). Crosses are calculations made by Smith *et al.* from their theory (see reference 27).

The resultant values for the collision diameter, b, are given in Table I.

The effect of temperature on the line width is also shown in these data. It should be emphasized, however, that these figures represent the variation of line width with temperature for constant pressure, since the absorption cell, at dry ice temperature, was connected to the filling system which was at room temperature. The filling system acted as a reservoir to maintain constant pressure.

For the estimation of errors in these measurements, in addition to random errors, it is necessary to consider effects resulting in systematic broadening. While the influence of modulation frequency and amplitude on observed line widths has been minimized, there may exist a broadening of not more than 2 percent. Other broadening up to 2 percent may result from the method of presentation of the line[16,17] and the proximity of harmonics of the measured line. However, there was observed no effect due to klystron sweep frequency or amplitude. The other errors involved are all of random nature; these errors, of amounts indicated, arise in frequency measurement by the receiver (1 percent), calibration of the receiver (primarily from interpolation of receiver dial settings) (1 percent), and the measurement of pressure (2 percent). Other random errors, estimated at 3 percent, may arise from the curvature of the klystron mode or from the small reflections present in the absorption cell. The total systematic error is then about 4 percent and the total random error, 7 percent. The errors are reported in percent because of the fact that the data were obtained by multiplying the measurements by the harmonic multiple of the klystron frequency. Thus the random error in the $J=3\rightarrow4$ measurement is 0.5 (Mc/sec) per mm and in the $J=13\rightarrow14$ measurement is 1.3 (Mc/sec) per mm.

INTERPRETATION

The interpretation of these experimental results has not been possible by any existing theory. The most rigorous theory available for explanation of self-broadening, that of Anderson,[4] shows that the line width, for linear molecules in low rotational quantum states, varies linearly with J. At higher rotational states this variation is less than linear because of the effect of the Boltzmann factor. Both the experimental results presented here and those of Johnson and Slager[11] show a quadratic variation of line width with J.

The simplified theory given by Smith and Howard[24] takes into account dipole-dipole and dipole-quadrupole interactions between molecules. According to their interpretation an interaction may only exist in the dipole-dipole collision if a symmetric- or asymmetric-top colliding molecule is involved, since only these molecules possess dipole moments when averaged over all orientations. While the self-broadening of linear molecules could not be accounted for by this interpretation, there exists the possibility of interpretation by a dipole-quadrupole interaction. In view of more recent experimental evidence presented by Benesch and Elder[25] this latter mechanism has not been invoked. Similarly the theory of Mizushima,[10] based upon quadrupole-quadrupole interaction, has not been used. This interaction, which is much smaller than dipole interactions, predicts a narrowing of the absorption line with higher rotational state.

Benesch and Elder report high-resolution measurements in the infrared region on foreign gas broadening of vibration-rotation lines of HCl and CH_4. While the spectra which they observe could not satisfy the Van Vleck-Weisskopf condition that the duration of the collision be short compared with the period of the incident radiation,[26] as well as not being similar in origin to microwave spectra, their Fig. 1. gives strong evidence for the fact that in the microwave and infrared regions collision broadening takes place by the same mechanism. They also present evidence in their Fig. 2 for the interpretation that, contrary to the results found by Anderson[4] and Smith,[24] dipole-dipole interactions are important in collision broadening, irrespective of the configuration of the broadening molecule. They conclude that: (1) at least two interactions are necessary to account for the broadening of a dipole absorber by a series of foreign broadening gases; (2) for foreign broadening gases which do not have dipole or quadrupole moments a polarizability interaction should be considered; (3) the broadening mechanism depends primarily upon a property of the broadening molecule and only to a lesser degree on one possessed by the absorbing molecule; and (4) for broadening molecules having quadrupole or dipole moments, the

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[24] W. V. Smith and R. R. Howard, Phys. Rev. **79**, 132 (1950).
[25] W. Benesch and T. Elder, Phys. Rev. **91**, 308 (1953).
[26] J. H. VanVleck and V. F. Weisskopf, Revs. Modern Phys. **17**, 227 (1945).

existence of strong broadening effects requires a more powerful interaction than polarizability forces between colliding molecules.

Recent theoretical work by Smith, Lackner, and Volkov[27] has shown that the magnitude of the self-broadening of OCS can be explained by a first-order dipole-dipole interaction using Anderson's[4] general theory. They indicate, however, that the observed temperature dependence of self-broadening must be accounted for with higher order interactions in addition to a dipole-dipole interaction of first order. These results are in agreement with the conclusions of Benesch and Elder.

Several examples of self-broadening now exist in the literature. All of these have shown self-broadening effects greater than their foreign broadening effects[28]; these molecules are: NH_3, OCS, HCN, ClCN, O_2, and HCl.[25] (The latter molecule has only been observed in the infrared; HCN has been observed in both the infrared and microwave regions.) To account for this anomalous behavior in NH_3 and O_2 resonance effects have been postulated.[4,5]

According to all collision broadening theories, collisions may be either weak or strong. The weak or adiabatic collision results from perturbations of the initial and final energy levels of the absorbing molecule produced by a Stark effect due to the proximity of the broadening molecule. A weak collision results in a phase shift of the radiation, thus broadening the line. The strong or nonadiabatic collision results from a complete interruption of the molecular absorption by having the absorbing molecule undergo an induced transition caused by collision with the broadening molecule. This type of broadening is explained by the Uncertainty Principle, since, in $\Delta E\Delta t \geqq \hbar$, the state lifetimes Δt are distributed statistically, resulting in a distribution of $\Delta E = h\Delta\nu$ for a line width.

For microwave broadening, only strong collisions need be considered.[24] This results from the explanations for saturation effects and also from the fact that no shift in frequency of the maximum of a microwave line occurs when pressure is increased. Frequency shifts, which occur in optical measurements, are characteristic of weak collision. Further evidence for the predominance of strong, transition-producing collisions is that the energy loss involved in an absorption is much less than the thermal energy of the molecule, that is, $h\nu \ll \frac{3}{2}kT$ for microwave spectra. Thus thermal collisions may involve relatively large energy transfers.

The explanation of the observed behavior of the line width as a function of J will be based upon the assumption of two contributing interactions, dipole-dipole and resonance. It will be assumed that the contributions to line width by dipole and other interactions are constant. Added to these contributions will be a resonance interaction term.

For the resonance term assume a collision-induced resonance transition. The lifetime of a molecule in the state J should be inversely proportional to the probability $B_{J\rightarrow J'=J\pm1}$ of a collision-induced transition and to the difference in the populations $N_J - N_{J'}$ of the initial and final states. The state lifetime is inversely proportional to line width,[26] so that the line width contribution due to resonance interaction may be expressed by

$$\Delta\nu_r = \text{const } B_{J\rightarrow J'}(N_J - N_{J'}). \tag{1}$$

The transition probability is given by[29]

$$B_{J\rightarrow J'} = \frac{8\pi^3}{3h^2}(J,M|\mu|J',M)^2.$$

Considering subsequently only the case where $J' = J+1$, the square of the matrix element is, for all orientations,[30]

$$(J,M|\mu|J+1,\,M)^2 = \mu^2(J+1)/(2J+1).$$

Thus the transition probability will be expressed by

$$B_{J\rightarrow J+1} = \frac{8\pi^3\mu^2}{3h^2}\left(\frac{J+1}{2J+1}\right). \tag{2}$$

The difference in the populations of the lower and upper states is given by the Boltzmann distribution in the approximate form[29]

$$N_J - N_{J'} \cong N_J h\nu_{J\rightarrow J'}/kT.$$

For a linear molecule the transition frequency is

$$\nu_{J\rightarrow J+1} = 2B(J+1).$$

The number N_J of molecules in the state J is given by the rotational Boltzmann distribution whose weight factor and state sum include the sum over all values of M (which was not included in the square of the matrix element),[31]

$$N_J = N(hB/kT)(2J+1)e^{-hBJ(J+1)/kT}.$$

Thus

$$N_J - N_{J'} \cong (2Nh^2B^2/k^2T^2) \times (J+1)(2J+1)e^{-hBJ(J+1)/kT}. \tag{3}$$

Substitution of Eqs. (2) and (3) into Eq. (1) gives the resonance term

$$\Delta\nu_r = \text{const } (J+1)^2 e^{-hBJ(J+1)/kT}. \tag{4}$$

A term of similar form is obtained for the transition $J \rightarrow J-1$.

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[27] Smith, Lackner, and Volkov, J. Chem. Phys. (to be published).

[28] Gordy, Smith, and Trambarulo, *Microwave Spectroscopy* (John Wiley and Sons, Inc., New York, 1953), pp. 192–193.

[29] See reference 28, p. 186.

[30] See reference 28, p. 201.

[31] G. Herzberg, *Spectra of Diatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1950), p. 125.

The line width may then be expressed by

$$\Delta\nu=\Delta\nu_d+\Delta\nu_r,$$

where $\Delta\nu_d$ is a constant representing the line width contribution resulting from the dipole-dipole interaction.

This resulting equation was found to fit well the dry-ice and room temperature data considered separately, but the temperature dependence indicated by Eq. (3) was not observed. For low J-values, where the resonance contribution is insignificant, the line widths at constant pressures are observed to follow an inverse temperature dependence.[12] For higher J-values the resonance term was found to vary as the square-root of the temperature. By empirical fitting of an equation, considering these temperature effects, it was found that the data for both temperatures was expressed by the general formula:

$$\Delta\nu=1815/T+0.00321T^{\frac{1}{2}}(J+1)^2e^{-hBJ(J+1)/kT} \quad \text{(Mc/sec) per mm.} \tag{5}$$

For comparison, Eq. (5) is plotted on Fig. 4 with the experimental data. No justification can be given for either temperature dependence.

The general form of Eq. (5), when extrapolated to high J-values, is seen to be similar to the experimental results obtained by Lindholm from the vibrational spectra of HCl and HCN.[32] The effect of the Boltzmann distribution is already indicated in the present data. The maximum line widths from Eq. (5) will occur at $J=24$ at 195°K and $J=31$ for 300°K.

There are indicated on Fig. 4 the four points calculated by Smith *et al.* from their rigorous theory.[27] There is excellent agreement between these values and the experimental data. It is hoped that their calculations will be extended to the higher J-values.

It is noteworthy that the collision diameters b of OCS, measured at constant pressure, are linearly dependent upon J and almost independent of temperature. The observed collision diameters are at least twice the kinetic theory diameters.[28]

It is a pleasure to acknowledge the aid and encouragement of Professor Walter Gordy in this work and the contribution of Charles A. Burrus, Jr., in obtaining the short-wavelength radiation necessary for these measurements. The author should like to express his gratitude to Professor William V. Smith for furnishing prepublication information on his theoretical work and for suggesting important corrections.

APPENDIX

The correction of observed line widths for the distortion in line shape produced by extreme absorption of the microwave energy will now be considered. The measurements of line width are made directly on the response of the crystal detector which indicates the loss in microwave power on transmission through the absorbing medium contained in the wave-guide cell. The method of correction has been given by Howard.[33] The absorbed power is expressed by

$$P=P_0(1-e^{-\alpha l}), \tag{6}$$

where P is the absorbed power; P_0, the incident power; l, the absorption cell length; and α, absorption coefficient is given by

$$\alpha=\alpha_0S=\alpha_0\frac{(\Delta\nu)^2}{\pi\Delta\nu[(\nu-\nu_0)^2+(\Delta\nu)^2]}. \tag{7}$$

Here α_0 is the peak absorption for the molecule; S, the Lorentz line shape factor; ν, the observation frequency; ν_0, the frequency of line center; and $\Delta\nu$, the line width.

For most measurements the exponential argument is small, so that the absorbed power is given by

$$P\cong P_0\alpha l=P_0\alpha_0Sl,$$

and the signal from the crystal detector is directly proportional to the Lorentz shape factor. Thus the line shape is undistorted. For a long absorption cell or for large α_0, this approximation is no longer valid and the exponential form must be used.

For a linear molecule the peak absorption coefficient is given by[34]

$$\alpha_0=\frac{4\pi^2\nu^3hN\mu^2}{3ck^2T^2}e^{-hBJ(J+1)/kT}. \tag{8}$$

Thus at high frequencies the peak absorption coefficient may become large.

The apparatus measures the frequency separation, $2\delta\nu$, of the inflection points of the absorption line, that is the points where

$$\partial^2P/\partial\nu^2=0. \tag{9}$$

However, it is desired to determine the line half-width at half-power, $\Delta\nu$, and thus it is necessary to determine the relations between observed $\delta\nu$ and the desired $\Delta\nu$. This may be derived by applying Eq. (9) to Eqs. (6), (7), and (8) and using series expansions on this result. The relation obtained is then

$$\Delta\nu=\sqrt{3}\delta\nu[1-\alpha_0l/4+(\alpha_0l)^3/128+\cdots].$$

It may then be shown by using only the first two terms, that the line width will be given by

$$\Delta\nu=\sqrt{3}\delta\nu-3.70\times10^{-10}(\nu^3\mu^2pl/T^3)e^{-hBJ(J+1)/kT}, \tag{10}$$

where ν is the transition frequency in Mc/sec; μ, the dipole moment of the molecule in Debye units; p, the pressure in mm Hg; and l, the absorption cell length in cm. This formula was used to obtain the corrections given in Table I.

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[32] See Figure 2 of reference 4a.

[33] R. R. Howard, Ph.D. thesis, Duke University, 1950 (unpublished).

[34] See reference 28, p. 186, 204–6.

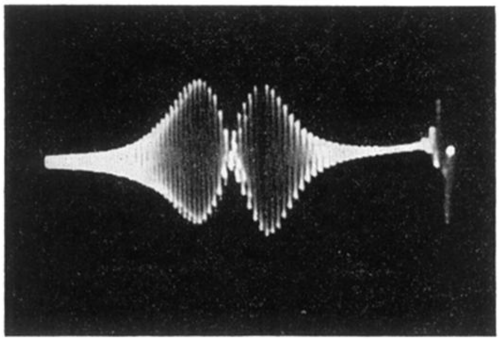

FIG. 2. Photograph of the cathode-ray oscilloscope presentation of the $J=7\rightarrow8$ transition occurring at 97 301.32 Mc/sec, the fourth harmonic of the klystron frequency.